Modeling and Optimization of Hydrogen Production from Gasification of Waste Polyethylene

by

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CERTIFICATION OF APPROVAL

MODELING AND OPTIMIZATION OF HYDROGEN PRODUCTION FROM GASIFICATION OF WASTE POLYETHYLENE

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MOHD SHAHRUL NIZAM B MOHAMMAD FADZILLAH

A project dissertation submitted to the
Chemical Engineering Programme
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(CHEMICAL ENGINEERING)

Approved by,

_____

(Dr Murni Melati Ahmad)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MOHD SHAHRUL NIZAM B MOHAMMAD FADZILLAH

ABSTRACT

Due to the energy crisis and environmental concern of fossil fuel usage, hydrogen has emerged as an alternative source of fuel. Hydrogen which is the major component of syngas, can be produced through gasification of waste polyethylene (PE). PE is a very sustainable source with a global production of 67 million tons in 2010. Waste PE catalytic steam gasification with in-situ carbon dioxide capture using CaO provides good prospects for the production of hydrogen rich gas. This work focuses on the process modeling and optimization for hydrogen production from waste PE using MATLAB. The model incorporates the reaction kinetics calculations of the steam gasification of waste PE with in-situ CO_2 capture, as well as mass balances calculations. The developed model is used to investigate the effect of temperature, type of catalyst and steam/PE ratio on the hydrogen purity and hydrogen yield. Based on the results, hydrogen purity of 35 mol% can be achieved. The maximum hydrogen yield predicted at the outlet of gasifier is 125gH_2/kg PE. It is also found that the increased in temperature and steam/PE ratio will enhance the hydrogen production. In conclusion, this work provided meaningful resources that can be used as a basis for more detail work for gasification of waste PE.

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(MOHD SHAHRUL NIZAM B MOHAMMAD FADZILLAH)

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

1.1.1 Hydrogen as Alternative Fuel

The energy crisis and environmental problems associated with the fossil fuel usage, led to the utilization of hydrogen as a clean and sustainable energy supply. Hydrogen fuel has gained increasing attention in energy sector because of its advantageous properties such as environmentally friendly combustion characteristics and high energy content. He et al. (2009) stated that hydrogen is used for methanol and ammonia synthesis; and hydrogen combustion engines to release its stored energy. It can also be converted to liquid transportation fuels using Fischer–Tropsch synthesis. Furthermore, it could be directly used in the production of electrical power in fuel cells or by combustion in gas turbines.

1.1.2 Waste Plastics as Alternative Source

The amount of plastic wastes produced that is increasing progressively year by year lead to the serious problem of its disposal. Tarmudi et al. (2009) estimated that Malaysia produced 1.78 million plastic wastes in 2010 where PE contributed to 60 % of that amount. Plastics do not readily biodegrade and can reside in a landfill for hundreds of years. Only a small percentage of plastic waste is recycled nowadays and the disposal process is mainly by landfill or incineration, both associated with environmental problems. According to He et al. (2009), plastics can be recycled by three different methods: mechanical recycling, chemical recycling and energy recovery. Only chemical recycling method, which converts waste plastics to useful hydrocarbons, has been

recognized as a promising approach. Gasification process, one of the chemical recycling techniques appears to be an interesting option in the development of full scale processes for the upgrading of solid wastes to more usable and energy dense materials.

In comparison, plastics have the advantage in terms of heating value compared to other cellulosic material. Wu and Williams (2010) reported that plastics have higher heating value and higher hydrogen content compared to biomass or some other municipal solid wastes; this ensures a higher hydrogen production from the gasification of plastics. Bockhorn et al. (1999) added that high energy content of polymers and the chemical composition of plastics are the factors for plastics waste to be considered as an additional resource of energy.

1.1.3 Conversion of Polyethylene into Hydrogen

PE is well known as the most common plastic. This substance is found in many ordinary household items, such as food wrap, shampoo bottles, milk containers, toys, and the common plastic bag used to tote groceries home from the store. Many research conducted had proved that gasification of waste PE can produce syngas, which primarily consists of hydrogen, carbon monoxide and carbon dioxide. Study by He et al. (2009) indicated that there is a strong potential for producing syngas from waste PE by a simple steam gasification process. In another study of co-gasification of biomass with plastic waste, Pinto et al. (2002) concluded that whenever there is shortness of biomass supplies, plastic waste can be substituted up to 60 % of the feed amount.

1.1.4 Gasification Process

Gomaa (2011) defined gasification as a process of heating-up of carbonaceous (carbon-based) raw material with some gasifying agent to produce gaseous fuel. The heating value of the gases produced from this process is generally low to medium. Gasification differs from combustion, where the fuel is combined with gasifying agent in a heated, pressurized vessel. The vessel is starved of oxygen to prevent or limit combustion,

creating partial oxidation of the fuel to produce syngas. In partial oxidation process, the gasifying agent could be steam, air or oxygen, or some mixture of two or more gasifying agents. The selection of gasifying agent is normally according to the desired chemical composition of the syngas and efficiency.

1.2 PROBLEM STATEMENT

The kinetics of PE gasification is limited due to several factors. The syngas produced from the gasification process contain carbon monoxide that is toxic to human being; and carbon dioxide which could harm the environment. Besides, there is also limitation in the parametric range. Gasification takes place at very high temperature usually in the range of 450 to 900℃, making it hazardous and costly. Therefore, computational approach is the best method to develop kinetic model.

1.3 OBJECTIVES

- To develop the process model on catalytic steam gasification of waste PE into hydrogen production based on the kinetics behavior.

- To investigate the effect of process variables such as feed physical conditions, amount of steam and operating temperature on the hydrogen purity and hydrogen yield.

- To solve for the optimum process conditions that give the minimum hydrogen production cost.

1.4 SCOPE OF STUDY

This work is mainly focused on the reactions and principles of pyrolysis and gasification process of waste PE. The significant of Le Chatelier principle of endothermic and exothermic reaction is important in the selection of temperature to achieve the optimum amount of product. Using the available data of past study, a kinetic model of gasification process is developed. The model prediction is first validated by simulation of MATLAB software using residual minimization before finding the optimum value of parameters. Flowsheet calculations of mass balance are included in this work to determine the final product yield. The optimization toolbox is also used to minimize the operation cost for hydrogen production.

CHAPTER 2

LITERATURE REVIEW

2.1 COMPOSITION OF WASTE POLYETHYLENE

The ultimate and proximate analysis of waste PE from He et al. (2009) is used as a reference for basic composition in the substance as shown in Table 2.1.

Table 2.1: Ultimate and proximate analyses of waste PE samples

Moisture content (wt %)	0.02
Proximate analysis (wt%, dry basis)	
Volatile matter	99.85
Fixed carbon	0
Fixed carbon	0.15
Ultimate analysis (wt%, dry basis)	
C	85.81
H	13.86
O	0
N	0.12
S	0.06
Low Heating Value (kJ/kg)	38.036
Apparent density (kg/m^3)	570.5

2.2 GASIFICATION OF POLYETHYLENE

He et al. (2009) stated that the gasification process of waste PE in the gasifier can be divided into two steps. The first step is pyrolysis, where thermochemical decomposition of PE with production of tar, char and volatiles occurred. It can be performed at a temperature of 300 – 700℃ or even higher. The second step is the reactions of CO, CO_2, H_2, and H_2O with the hydrocarbon gases and carbon in waste PE feedstock, thereby producing the final form of gaseous product. In another study, Wu and Williams (2009) also divided this process in two stages. The two stages pyrolysis-gasification system consists of a first stage pyrolysis reactor heated by a tube furnace and a second gasification reactor separately heated by a second tube furnace. The waste plastics are placed in the first reactor at the beginning. The pyrolysis gases then flow to the second reactor containing the catalyst, where the steam is introduced and reforming reactions is carried out.

Sekiguchi and Orimo (2004) stated that most processes of gasification and pyrolysis of PE are carried out with a fluidized bed reactor due to its high heat transfer characteristics. Pinto et al. (2002) also agreed that fluidized bed steam gasification has been proven as a possible way of converting biomass and plastic wastes into fuel gases. He et al. (2009) added that gasification reaction takes place on the surface of solid catalysts. Usually nickel supported catalysts are used in this process. Nickel supported catalyst are chosen due to its high effectiveness in tar removal along with the added advantages of methane reforming and water gas shift activity, allowing adjustment of the H_2/CO ratio of the product gas.

Pinto et al. (2002) had chosen steam as gasifying agent for gasification process instead of oxygen and air. It comes with the purpose of reducing the diluting effect of N_2 from air and eliminating the need for an expensive O_2 plant. Inayat et al. (2012) also found that the use of pure steam as the gasification agent for hydrogen production is not only in favor of higher hydrogen production but also is more economical than other conventional gasifying agents and pyrolysis.

Sadaka (n.d.) reported that gasification of solid waste with reactive gases such as steam and CO_2 as well as secondary reactions such as the water gas shift reaction, methanation and reforming of tars are normally favored at high temperatures (>600℃). Normally, the char-gas reaction will control the conversion of the char; therefore their products can dominate the final gases product. The composition of the final product gas can be determined by the degree of equilibrium attained by various gas phase reactions.

The heterogeneous reactions occur in a gasifier and their standard enthalpy changes by Sadaka (n.d.):

$C + CO_2 \rightarrow 2CO$ +173.0 kJ/mol (1)

$C + 2H_2 \rightarrow CH_4$ -71.0 kJ/mol (2)

$C + H_2O \rightarrow CO + H_2$ +131.4 kJ/mol (3)

The gas phase reactions (homogenous) occur in a gasifier and its standard enthalpy change by Sadaka (n.d.):

$CO + H_2O \rightarrow CO_2 + H_2$ - 41.2 kJ/mol (4)

$CH_4 + H_2O \rightarrow CO + 3H_2$ -201.9 kJ/mol (5)

According to Swierczynski et al. (2007), one of the most crucial problems in gasification technology is the removal of tar, which is a mixture of condensable aromatic compounds. There is a possibility for tar to condense or polymerize into more complex structures in equipments such as exit pipes, heat exchangers or on particulate filters, leading to choking and attrition. Therefore, it is necessary to eliminate tar from the gasification product before additional usage in any application. Tar removal technologies can be divided into two approaches. The primary method is treatments inside the gasifier such as proper selection of operating parameters, use of bed additive/catalyst and gasifier modifications. The secondary methods is hot gas cleaning after the gasifier which include tar cracking, either thermally or catalytically, or mechanical separation using

cyclones, filters or scrubbers. Coll et al. (2001) reported that catalytic steam reforming has been proven effective to eliminate tar component. The process of steam reforming involves oxidation of the tar components using steam to produce hydrogen and carbon oxides where it is usually carried out with supported nickel-based catalysts at temperatures of between 650 and 900°C. The reaction pathway can be described with reaction:

$$C_xH_y + H_2O \rightarrow CO + (x+y/2)\, H_2 \quad (6)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Toluene was selected as the model tar compound as it represents a stable aromatic structure found in tar formed during gasification process. Because of the complexity of the gasification gas product, many parallel and consecutive reactions can take place. In order to simplify the model, Swierczynski et al. (2007) concluded that toluene reacted principally with water to produce hydrogen and carbon monoxide:

$$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2 \quad (\Delta H_{298\,K} > 0) \quad (7)$$

In this work, Calcium Oxide is also used as the adsorbent for in-situ CO_2 capture. Wang (2012) stated that CO_2 adsorption for enhancement of gasification process is one of the prospective technologies to be used in hydrogen production with nearly zero CO_2 emission. Inayat (2012) also agreed that the purity of hydrogen in the product gas can be further increased with in-situ CO_2 capture technique using Calcium Oxide as the sorbent. The carbonation reaction can be described as:

$$CaO + CO_2 \rightarrow CaCO_3 \qquad -178.3\ kJ/mol \quad (8)$$

The reaction rates for all the reactions are considered to have first order and Arrhenius type temperature dependence.

2.3 PARAMETRIC STUDY FOR GASIFICATION OF WASTE PE

2.3.1 Temperature

Pinto et al. (2002) claimed that for temperature range of 730-830℃, apart from the reforming and cracking reactions, the water gas shift reaction was probably one of the most important reactions for reaching final gas composition. This reaction also releases CO_2 besides H_2. The concentration of CO_2 increased until temperature of 830℃ but decrease in higher temperature. It is predicted that reactions that consume CO_2 become more dominant, probably Boudouard reaction. He also added that water gas shift reaction might be less important than Boudouard and water gas reaction for higher temperature. He et al. (2009) suggested that according to Le Chatelier's principle, higher temperature favor the reactants in exothermic reactions and favor the products in endothermic reactions. Water gas shift reaction is exothermic and thus less important at higher temperature. He concluded that at higher temperature; Boudouard, water gas and methane decomposition reaction were the main factors responsible for the increase in H_2 and CO contents.

2.3.2 Catalyst

According to He et al. (2009), NiO/γ-Al_2O_3 catalysts were used in steam gasification processes of waste PE to enhance the yield and quality of product gas and decrease tar yield. Presence of NiO/γ-Al_2O_3 catalysts can increase H_2 and CO_2 content, while CO, CH_4, C_2H_4 and C_2H_6 contents diminished. In another study, Wu and Williams, (2010) conclude that presence of Ni-Mg-Al catalyst in the gasification bed increase the H_2 production from 0.015g H_2/g waste plastics to 0.258 g H_2/g waste plastics. Swierczynski et al. (2007) also reported that Ni/olivine catalyst is efficient in tar removal from gasification gas by using a model of toluene steam reforming. At temperature higher than 650℃, total toluene conversion is obtained and carbon formation is negligible. H_2

and CO are the main gaseous reaction products which having proportions in good agreement with thermodynamic equilibrium.

2.3.3 Steam/PE ratio

This parameter is compared based on steam/biomass ratio due to insufficient information for steam/PE ratio. According to Ahmed et al. (2011), in study of gasification of palm kernel shell, increase in steam/biomass ratio enhances hydrogen production attributed to the utilization of the hydrogen content of steam in the reforming and shift reactions. Nevertheless, Inayat et al. (2012), in study of gasfification of oil palm empty fruit bunch claimed that hydrogen efficiency decreases by increasing steam/biomass ratio as more energy is required for additional steam usage despite the increased hydrogen yield. In study of co-gasification of biomass with waste plastic, Pinto et al. (2002) stated that the gasification process was not much affected by the range of steam/waste ratios tested. However, the ratios should not be lower than 0.6 because low steam amount is not enough for the gasification process.

2.4 PROCESS DEVELOPMENT

A simplified process has been developed by Inayat et al. (2012) for the hydrogen gas production by gasification process. The block diagram of the process is shown in Fig. 2.3. The whole process consists of five main sections which are feed treatment, steam generation, gasification, regenerator and gas cleaning units. Waste PE is treated prior to gasification which consists of drying and size reduction. The process design also includes a steam system that consists of a steam generator that produces saturated steam and steam-superheaters that produce superheated steam. The adsorbent, CaO is regenerated from calcination of $CaCO_3$ in a regenerator using external heat. The product gas contains of hydrogen, carbon monoxide, carbon dioxide and methane along with steam and fly ash. In order to obtain pure hydrogen as the end product, several steps of

gas cleaning are incorporated. The product gas was cooled down and steam was removed by passing it through scrubber with fresh water. The pressure swing adsorption (PSA) unit is then utilized to get hydrogen of 99.99% purity.

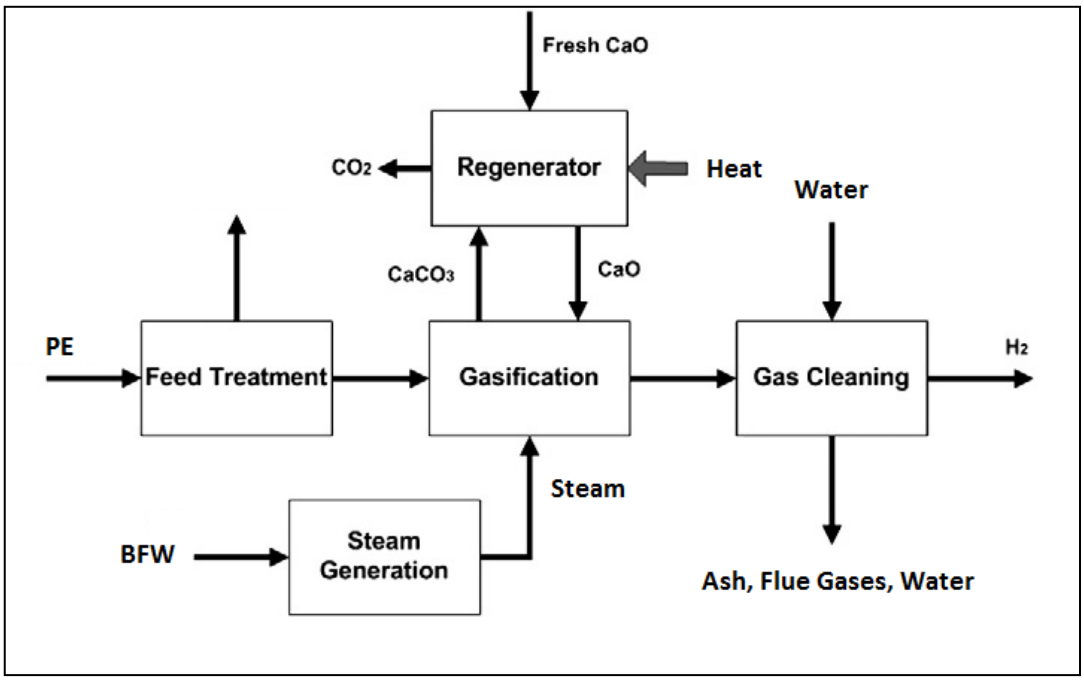

Figure 2.3 Block diagram of the gasification process (Inayat et al. (2012))

CHAPTER 3

METHODOLOGY

3.1. RESEARCH FLOW

This work is started by collecting information of the reaction scheme for gasification process. Next, the reaction model is developed for hydrogen production for steam gasification of waste PE. The final value of model is fitted with past study reported for validation by using MATLAB. Once the model has been validated, parametric study on hydrogen purity and hydrogen yield with respect to temperature and steam/PE is done. Next, mass balances for the whole process are calculated. Cost calculation and cost minimization is performed to find the optimum condition that could give lowest price of hydrogen production. Flowchart for this work is shown in Figure 3.1.

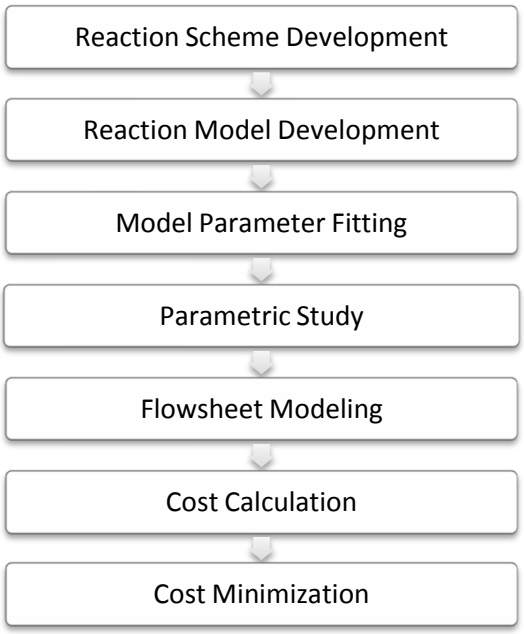

Figure 3.1: Research flow

3.1.1 Reaction Scheme Development

The reaction scheme for gasification of waste PE is shown in Table 3.1.2:

Table 3.1.1 Reaction scheme

No	Name	Reaction
1	Steam tar reforming	$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2$
2	Char gasification	$C_{20}H_{40} + 20H_2O \rightarrow 20CO + 40H_2$
3	Methanation	$C_{20}H_{40} + 20H_2 \rightarrow 20CH_4$
4	Methane decomposition	$CH_4 + H_2O \rightarrow CO + 3H_2$
5	Water-gas shift (forward)	$H_2O + CO \leftrightarrow H_2 + CO_2$
6	(reverse)	
7	Carbonation	$CaO + CO_2 \rightarrow CaCO_3$
8	Boudouard	$C_{20}H_{40} + 40CO_2 \rightarrow 60CO + 20H_2O$

3.1.2 Reaction Model Development

Based on the list of reaction scheme, reaction kinetics model can be created as follow:

- First order with respect to reacting species

$$k_i = A_i exp^{-E_i/RT} \quad i = 1,2,3,4,5,6,7,8 \tag{9}$$

$$r_i = k_i C_A C_B \tag{10}$$

- The overall volumetric rate of each component

$$R(H_2) = 11r_1 + 40r_2 - 20r_3 + 3r_4 + r_5 - r_6 \tag{11}$$

$$R(CO) = r_1 + 20r_2 + r_4 - r_5 + r_6 + 60r_8 \tag{12}$$

$$R(CH_4) = 20r_3 - r_4 \tag{13}$$

$$R(CO_2) = r_5 - r_6 - r_7 - 40r_8 \tag{14}$$

The overall chemical reactions considered in the model and their kinetics constant values are listed in Table 2.2.

Table 2.2 Chemical reactions considered in the model

No	Name	Reaction	Kinetics Constant	Basis	Reference
1	Boudouard	$C_{20}H_{40} + 40CO_2 \rightarrow 60CO + 20H_2O$	247 exp (-21060/T)	Coal	Choi et al. (2001)
			4.40 exp (-1.62×10^{8}/T)	Biomass	Inayat et al. (2009)
2	Methanation	$C_{20}H_{40} + 20H_2 \rightarrow 20CH_4$	0.12 exp (-17921/T)	Coal	Choi et al. (2001) Zhao et al. (2008)
3	Char gasification	$C_{20}H_{40} + 20H_2O \rightarrow 20CO + 40H_2$	247 exp (-21060/T)	Coal	Zhao et al. (2008)
			2.0×10^{5} exp (-6000/T)	Biomass	Inayat et al. (2009)
4	Methane decomposition	$CH_4 + H_2O \rightarrow CO + 3H_2$	$3.15\text{x}10^{2}$ exp (-15000/T)	Biomass	Corella and Sanz (2005) Zhao et al. (2008)
5	Water-gas shift	$H_2O + CO \leftrightarrow H_2 + CO_2$	T<1123 °C 10^{6} exp (-6370/T) $K_W = 520\text{x}10^{-3}$ exp (-7230/T)	Biomass	Corella and Sanz (2005) Inayat et al. (2009)
6	Carbonation	$CaO + CO_2 \rightarrow CaCO_3$	10.20 exp (-44.5/T)	Biomass	Ar and Dogu (2001) Yunus et al. (2009)
7	Steam tar reforming	$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2$	3.14×10^{13} exp (-23575/T)	Biomass	Swierczynski et al.(2007)

3.1.3 Model Parameter Fitting

The next step is parameter fitting of reaction model. Generally, kinetics modeling allows predicting the process performance in terms of product gas composition. However, one prominent challenge in kinetics modeling is rate parameters data reported in literature are usually from gasification of either coal or various types of biomass. Because of the difference in composition of lignocellulosic components of every biomass or coal, the use of similar reported rate parameters data for the purpose of predicting performance of gasification of a certain biomass maybe affect the value of final product. Hence, to solve this problem, it is crucial to construct an optimization approach to estimate the kinetics parameters for the steam gasification of waste PE. The Minimum Residual Error is used to calculate the kinetics parameter for gasification of PE by comparing the model predictions with experimental values. The method is shown in Figure 3.1.3.

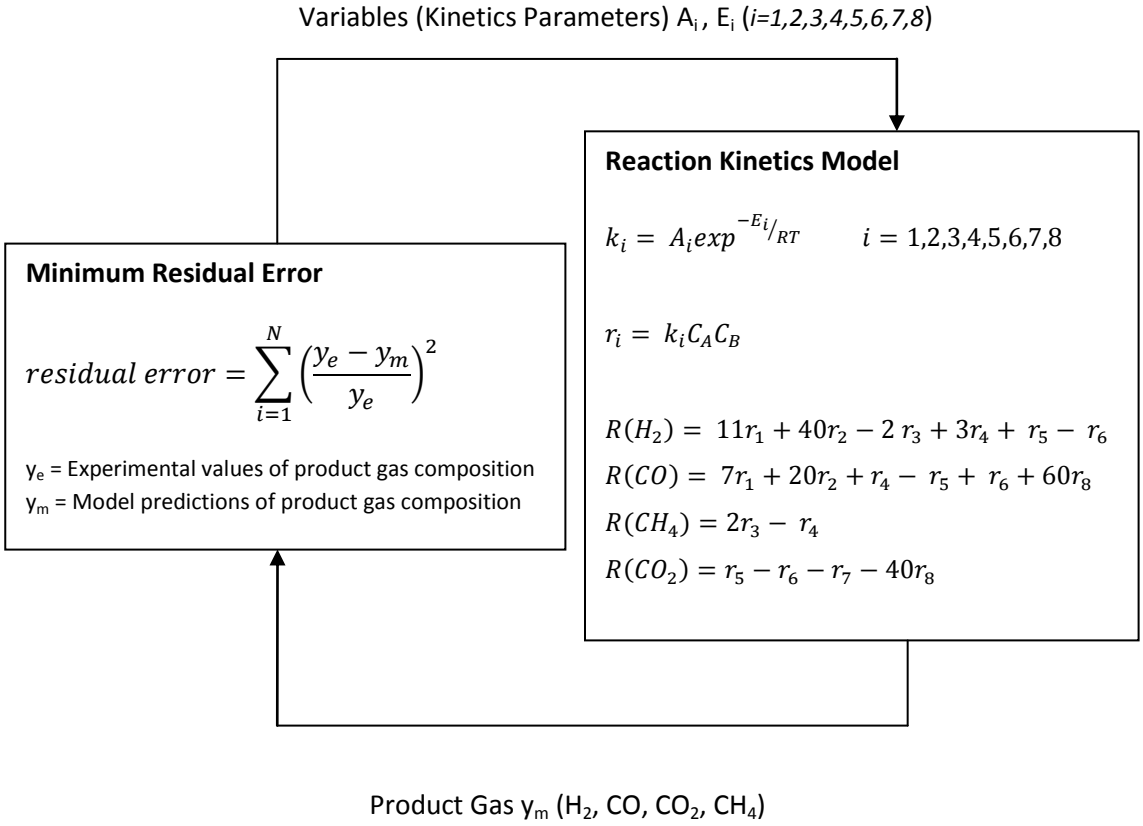

Figure 3.1.3: Parameter fitting approach

3.1.4 Parametric Study

The temperature and steam/PE ratio is studied to determine the effect result is represented on a graph of hydrogen yield and hydrogen purity.

3.1.5 Flowsheet Modeling

Model equations in this work include:

- Mass Balance

$$\sum_i m_i = \sum_o m_o \quad (15)$$

Where: m_i = Mass Flow Rate In
m_o = Mass Flow Rate Out

- Energy Balance

$$H_{PE} + H_{H_2O} + H_{CaO} + Q_{EE} = H_{H_2} + H_{CO} + H_{CO_2} + H_{CH_4} + H_{H_2O} + H_{CaCO_3} \quad (16)$$

- Enthalpy

$$H = n \times (H_f + \Delta H) \quad (17)$$

$$\Delta H = \int_{T_1}^{T_2} C_P dT \quad (18)$$

Where: H = Enthalpy
H_f = Standard Enthalpy of Formation
C_p = Specific Heat Capacity
n = No. of Moles

- Hydrogen Yield

$$Hydrogen\ Yield = \frac{Hydrogen\ yield\ in\ the\ gasifier\ (g)}{PE\ feed\ into\ the\ gasifier\ (kg)} \quad (19)$$

- Hydrogen Purity

$$Hydrogen\ Purity = \frac{Mol\ of\ hydrogen}{Total\ mol\ composition\ of\ gases} \times 100 \quad (20)$$

3.1.6 Cost Calculation

The cost is calculated based on the total capital investment which includes equipments and feed materials such as PE, steam, sorbent and catalyst.

- Purchased Equipment Cost (Guthrie's Cost Correlation)

$$Gasifier\ cost = \left(\frac{M\&S}{280}\right) \times 101.9 \times \left({D_G}^{1.066}\right) \times \left({H_G}^{0.82}\right) \times F_{C(Gasifier)} \quad (21)$$

$$Cyclone\ cost = \left(\frac{M\&S}{280}\right) \times 101.9 \times \left({D_C}^{1.066}\right) \times \left({H_C}^{0.82}\right) \times F_{C(Furnace)} \quad (22)$$

$$Scrubber\ cost = \left(\frac{M\&S}{280}\right) \times 101.9 \times \left({D_S}^{1.066}\right) \times \left({H_S}^{0.82}\right) \times F_{C(Scrubber)} \quad (23)$$

$$PSA\ cost = \left(\frac{M\&S}{280}\right) \times 101.9 \times \left({D_{PSA}}^{1.066}\right) \times \left({H_{PSA}}^{0.82}\right) \times F_{C(Scrubber)} \quad (24)$$

Where: (M&S) value for year 2012 is 1504.8

V = $(F_L/\rho_L \times \tau)\ 2$
D = $(V/\pi)^{1/3}$
H = 4D

D = Diameter of equipment
H = Height of equipment
V = Liquid holdup
ρ = Density of flow
F_L = Flow rate

F_c = Materials and pressure factors for equipment
For pressure vessel:
F_c = Fm.Fp
F_m = Material factor (Carbon steel = 1.0)
F_p = Pressure factor (Assume = 1.0)
Source: Perry's Handbook (2008)

- Cost Estimation

$$Cost\ of\ hydrogen\ production = \frac{Total\ Cost}{Total\ Hydrogen\ Produced} \quad (25)$$

$$\boldsymbol{Total\ Cost\ (TC)} = \sum Total\ capital\ investment\ (TCI) + \sum Total\ product\ cost\ (TPC) \quad (26)$$

$$\boldsymbol{Total\ capital\ investment\ (TCI)} = \sum Fixed\ capital\ investment\ (FCI) + \sum Working\ capital\ (WC) \quad (27)$$

$$Fixed\ capital\ investment\ (FCI) = \sum Direct\ cost\ (DC) + \sum Indirect\ cost\ (IC) \quad (28)$$

$$Direct\ cost\ (DC) = Distribution\ factor\ for\ direct\ cost \times \sum Purchased\ equipment\ cost\ (PEC) \quad (29)$$

$$Indirect\ cost\ (DC) = Distribution\ factor\ for\ indirect\ cost \times Direct\ Cost \quad (30)$$

$$Working\ Capital\ (WC) = Correlation\ of\ working\ capital \times Fixed\ capital\ investment \quad (31)$$

Where: Distribution factor for direct cost = 0.92
Distribution factor for indirect cost = 0.05
Correlation of working capital = 0.2
Source: Inayat et al. (2012)

$$\boldsymbol{Total\ product\ cost\ (TPC)} = \sum Total\ direct\ production\ cost\ (TDPC) + \sum Total\ manufacturing\ cost\ (TMC) + \sum Total\ general\ expenses\ (TGE) \quad (32)$$

$$Total\ Direct\ Production\ Cost = PE\ cost + Sorbent\ cost + Catalyst\ cost + Maintenance\ \&\ Repair \quad (33)$$

$$Total\ Manufacturing\ Cost = Local\ tax + Insurance + Interest + Plant\ Overhead \quad (34)$$

$$Total\ General\ Expenses = Administration + Distribution\ \&\ Selling + R\&D \quad (35)$$

Where: PE cost = 0.15 USD/kg (Recycler's World)
Sorbent cost = 0.1 USD/kg (quotation UNiversal)
Catalyst cost = 0.2 USD/kg (Euramco (M) Sdn Bhd)

Maintenance & repair	= 2% FCI
Local Taxes	= 1% FCI
Insurance	= 1% FCI
Interest	= 7% FCI
Plant overhead cost	= 7% FCI

Source: Inayat et al. (2012)

$$\boldsymbol{Total\ Hydrogen\ Produced} = H2 \times 20\ years \times 335\ days \times 12\ hours \quad (36)$$

3.1.7 Cost Minimization

The minimization of hydrogen production cost is performed in MATLAB software which is called *fmincon.* It is to solve for the optimum process condition that give the minimum hydrogen cost production. The cost minimization step is shown in Figure 3.1.7.

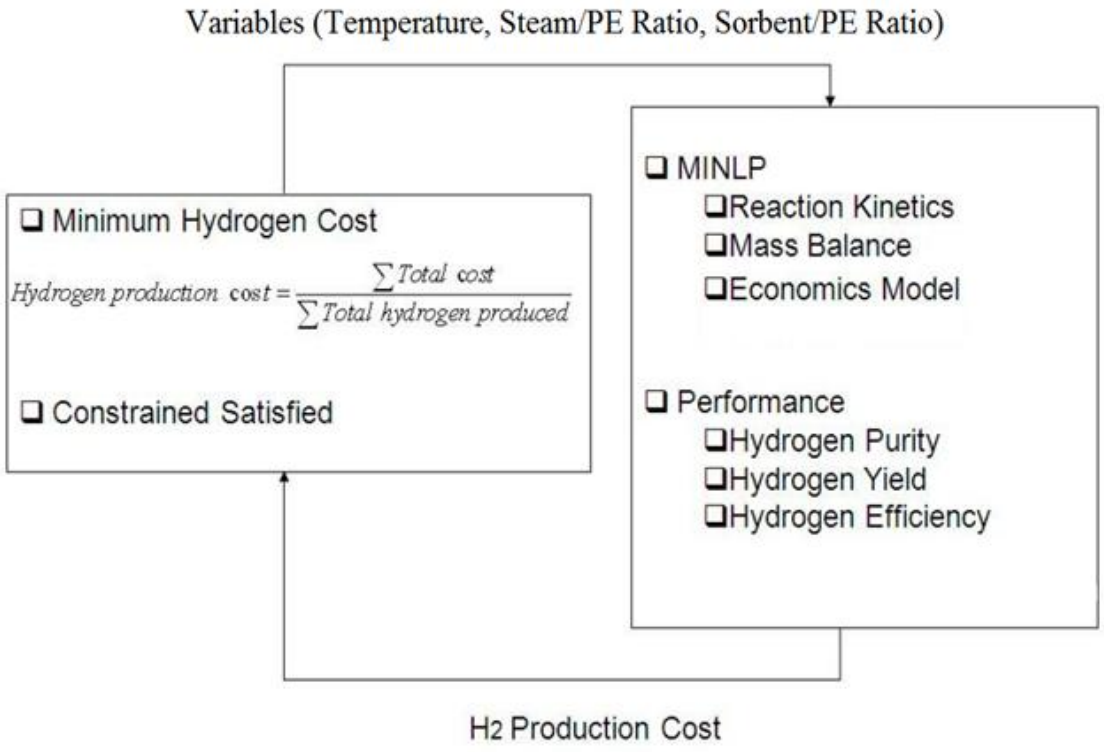

Figure 3.1.7: Cost minimization

The constraints of parameters need to be satisfied in this work are:

$973 \leq T \leq 1023$

$0.6 \leq$ Steam/PE ≤ 1.33

$0.8 \leq$ Sorbent/PE ≤ 1.0

Hydrogen Purity $\geq 35\%$

Hydrogen Yield ≥ 120

3.2 KEY MILESTONE & GANTT CHART

For FYP 2, key milestone and Gantt chart is shown in Table 3.2

Table 3.2.1: Gantt chart for FYP 1

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Reaction Scheme Development														
2	Reaction Model Development														
3	Model Parameter Fitting														
4	Parametric Study														
5	Flowsheet Modeling														
6	Cost Calculation														
7	Cost Minimization														

Table 3.2.2: Gantt chart for FYP 2

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Reaction Scheme Development														
2	Reaction Model Development														
3	Model Parameter Fitting														
4	Parametric Study														
5	Flowsheet Modeling														
6	Cost Calculation														
7	Cost Minimization														

CHAPTER 4

RESULT AND DISCUSSION

4.1 KINETICS MODEL DEVELOPMENT

An optimization model is used to calculate the kinetics parameters for the gasification process via fitting the model prediction on the product gas compositions with another experimental study. The optimization is performed using a built-in numerical optimizer in MATLAB software called *fmincon*. It minimizes the residual between model prediction values and the experimental data by changing values of kinetic rate parameters until a desired deviation tolerance is achieved. The final result of this section is shown in Table 4.1.

Table 4.1 Kinetics Parameters

No	Name	Kinetics Constant (s^{-1})	
1	Steam-tar	99736 exp (-15329/T)	
2	Char gasification	6302 exp (-12809/T)	
3	Methanation	2.07×10^{-3} exp (10303/T)	Minimum value of objective function = 0.04
4	Boudouard	37.017 exp (-5019/T)	
5	Methane reforming	98 exp (-19816/T)	
6	Water gas shift (forward) (reverse)	2481exp (-18337/T) 0.113 exp (16124/T)	
7	Carbonation	1.224 exp (3624/T)	

The minimum value of objective function is calculated by using minimum residual error (MRE). The value of MRE obtained in simulation is 0.04. It is in the acceptable range.

4.2 DATA VALIDATION

The value obtained in the Model Parameter Fitting is then compared to the experiment value for validation. The result is shown in Figure 4.1.

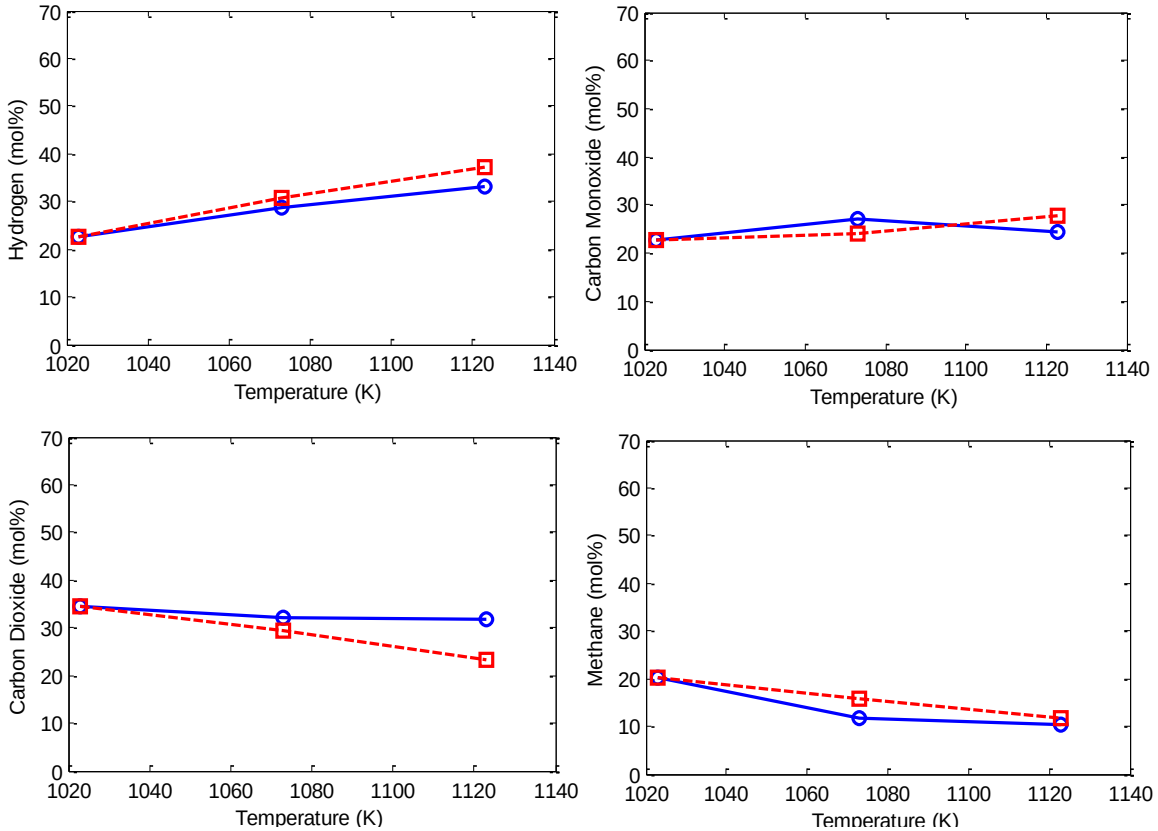

Figure 4.1: Data Validation. Mod (○), Exp (□) He et al. (2009)

Based on the Figure 4.1, as the temperature increase within the range, H_2 and CO concentrations increase while CO_2 and CH_4 concentrations decrease. The composition for each component of gases is compared with the results reported by other researchers on steam gasification of waste PE. The trends of current study are in agreement with study reported by He et al. (2009).

It is important to relate this result according to the Le Chatelier's principle which stated that higher temperatures favor the reactants in exothermic reactions and favor the products in endothermic reactions. Endothermic behavior of char gasification (3) and

methane reforming (5) is one of the factors contributing to high composition of hydrogen in product gases. The usage of steam and CO produced via char gasification also promotes the water gas shift reaction (4), which consumes CO and produces H_2 and CO_2. In this specified range of temperature, water gas shift reaction was probably one of the most important reactions that dictate the final gas composition. The trends of gases in the graph simply explained the water gas shift reaction itself where H_2 and CO_2 increased while CO decreased as the temperature rising.

Methane reforming may also important when higher amounts of PE were used, as the cracking of PE polymeric structure could lead to the formation of methane by methanation reaction (2), which would further react in methane reforming reaction which produced three hydrogen molecules. The used of CaO for carbonation reaction (8) also contribute to increase in hydrogen yield. The function of CaO is to acts as a catalyst as well as the CO_2 sorbent, which lowers the partial pressure of CO_2, and pushes the equilibrium of the water gas shift reaction forward.

4.3 PARAMETRIC STUDY

The result of hydrogen yield with respect to the temperature and steam/PE is presented in Figure 4.3.1.

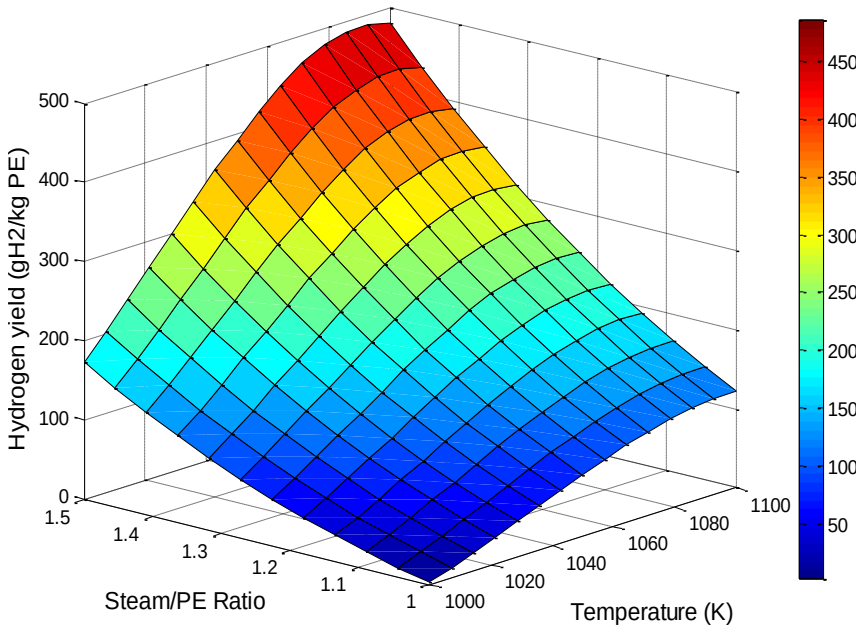

Figure 4.3.1: Hydrogen Yield

Hydrogen yield is the final amount of hydrogen gas produced after several steps of purification. Based on Figure 4.3.1, hydrogen yield increased when temperature and steam/PE ratio increased.

According to Arrhenius equation (9), reactions proceed rapidly as the temperature increases. The result has proved that temperature plays a significant role in determining the final concentration of product. This equation can be related to the collision theory. It stated that the molecules that collide must have minimum kinetic energy required for the collision and correct orientation to yield a successful reaction. Thus, temperature will play an important role for this requirement. Kinetic theory states that increased temperature makes the molecules accelerate; thus there's more chance of a collision. Since the molecules are moving faster at high temperatures, the amount of energy

generated on impact is more than enough to sustain a successful product. Therefore, the reaction rate would increase and resulted in higher hydrogen yield.

The result of hydrogen purity with respect to the temperature and steam/PE is presented in Figure 4.3.2.

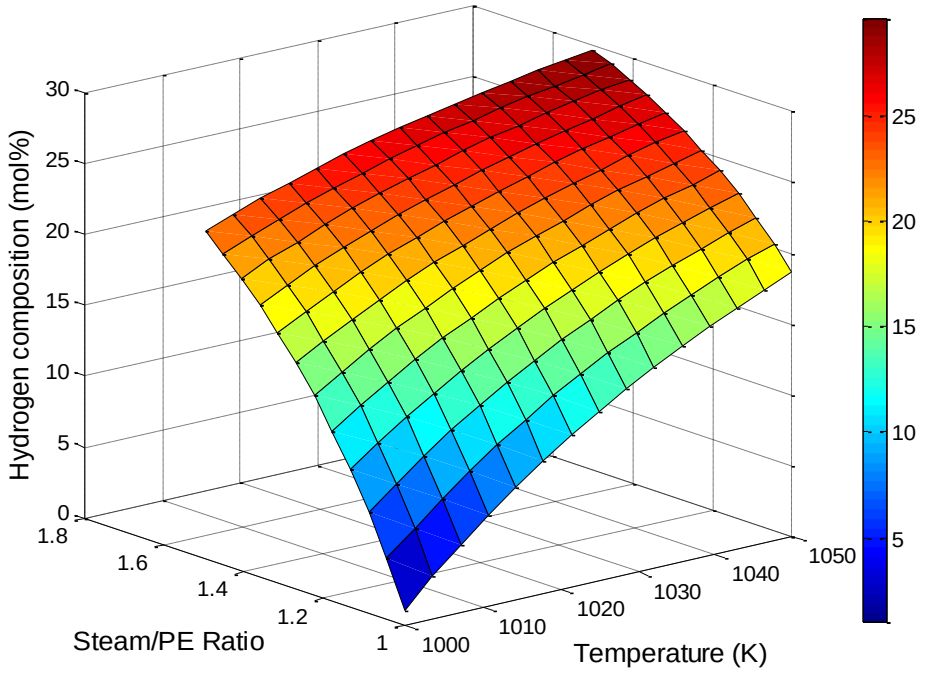

Figure 4.3.2: Hydrogen Purity

Hydrogen purity is the mol composition (mol %) of hydrogen gas at the outlet of gasifier. Based on Figure 4.3.2, hydrogen purity increased when temperature and steam/PE ratio increased.

For gasification of waste PE, water gas shift (WGS) reaction can be considered as the major reaction in determining the final product. It is related to the rate of reaction (10) where the amount of steam used for WGS reaction alone is half from the total steam supplied. This will ensure high concentration of product from this reaction, which is hydrogen and carbon monoxide. Besides, CO concentration is consistently reduced due to the excess steam, which shifts the equilibrium reaction of water gas shift reaction forward.

Water Gas Shift reaction: $H_2O + CO \leftrightarrow H_2 + CO_2$

Pinto et al. (2002) also agreed that for temperature range of 730-830℃, the WGS reaction was probably one of the most important reactions for reaching final gas composition. Therefore, the increased of steam/PE ratio will result in higher hydrogen composition or purity in gas component for gasification process. However, Li et al. (2009) reported that when there is too high ratio of steam/PE, the hydrogen concentration decreased. The introduction of more steam in fixed bed gasifier will lower down the reaction temperature and result in low H_2 production.

4.4 MASS BALANCES

The mass balances for the overall process is done at operating condition of 1013K, steam/PE ratio of 1.3 and sorbent/PE ratio of 0.5. The calculation is shown in Figure 4.4.

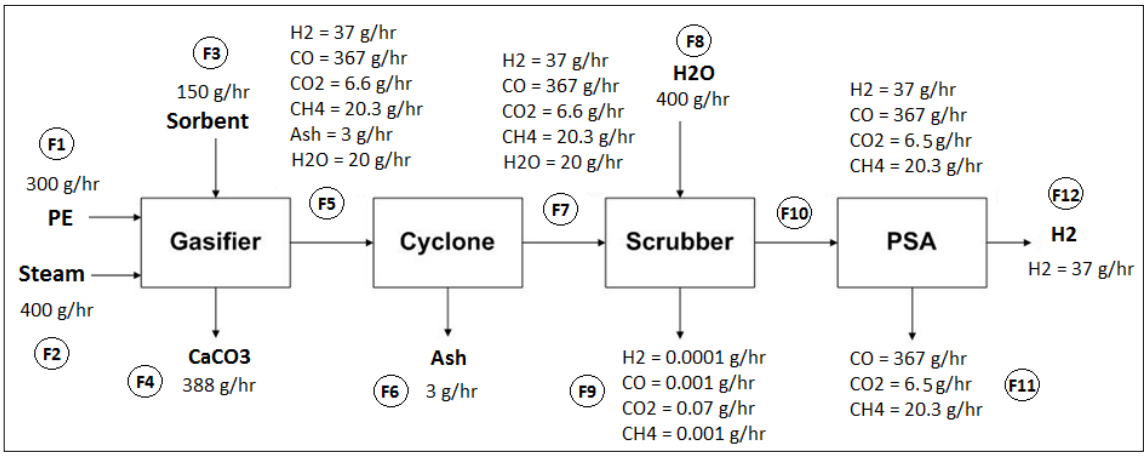

Figure 4.4: Mass Balances Flow Sheet

Based on the Figure 4.4, the feed component for this process are PE, steam and sorbent with the amount of 300g/hr, 400g/hr and 150g/hr respectively. The gasification reaction that occurred in the gasifier produced gases such as hydrogen, carbon monoxide, carbon dioxide, methane, steam and ashes. In the present of sorbent, carbon dioxide amount is reduced due to the carbonation reaction which later produced calcium carbonate.

Gomaa (2011) stated that amount of ash produced by gasification of plastics is only 1% from the feed. The ash is removed from the system by using cyclone. Next, scrubber is used to separate water from the gases component. In this process, there are some portions of the gases that dissolved in the water. The solubility of gases in water is shown in Table 4.4.

Table 4.4: Solubilities of Gases in Water

Gas	**Solubility***
Hydrogen	0.00016
Carbon monoxide	0.0028
Carbon dioxide	0.169
Methane	0.0023

*Grams of gas dissolved in 100 g of water when the total pressure above the solution is 1 atm. Kaye and Laby, (1986).

The gases components then exit through the top of the scrubber while water and soluble gases at the bottom. The last equipment used in this process is pressure swing adsorption, (PSA). The main function of PSA is to separate hydrogen from other component of gases. In this work, PSA is assumed to operate in 100% efficiency. The final amount of hydrogen gas produced after the PSA is 37g/hr. This is equivalent to 123gH_2/kg PE.

4.5 COST CALCULATION

The values of cost calculation for equations (21) - (36) are shown in Table 4.5.

Table 4.5 Cost Calculation

Item	Price (USD)
Gasifier	2274
PSA	480
Scrubber	378
Cyclone	126
Purchased Equipment Cost	3258
Fixed Capital Investment	3147
Working Capital	629
Total Capital Investment	3777
Total Direct Production Cost	6334
Total Manufacturing Cost	504
Total General Expenses	283
Total Product Cost	7121
Total Cost	10897
Total Hydrogen Produced	2924

$$\text{Cost of hydrogen production} = \frac{\text{Total Cost}}{\text{Total Hydrogen Produced}}$$

$$= 3.7 \text{ USD/kg } H_2$$

4.6 COST MINIMIZATION

The result for cost minimization is shown in Table 4.6.

Table 4.6: Optimum condition

T (K)	Steam/PE	Sorbent/PE	Cost (USD/kg H_2)
1014	1.33	0.4	3.5

The result of mass balances at optimum condition is shown in Figure 4.6.

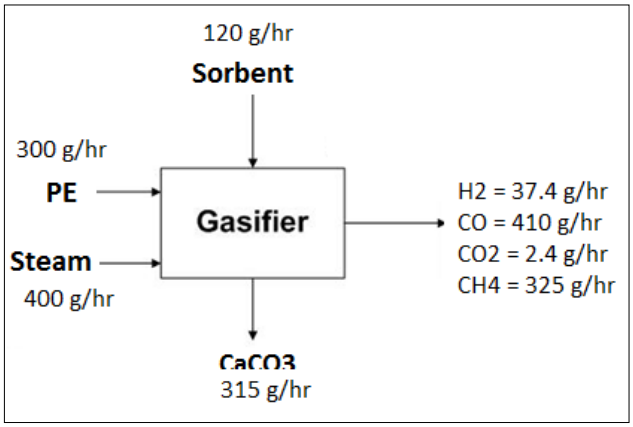

Figure 4.6 Mass balances at optimum condition

At optimum condition, the hydrogen yield of 125gH_2/kg PE; and hydrogen purity of 35% can be achieved. The result is acceptable since the hydrogen yield and hydrogen purity at desired value can be obtained at 3.5 USD/kg PE. Another study in gasification of effluent fruit bunch (EFB) by Inayat et al. (2012) reported hydrogen production of 158g/kg EFB with cheaper production cost of 1.32 USD/kg PE. The different in production cost in mainly due to the higher price of waste PE compared to the EFB.

CHAPTER 5

CONCLUSION

A process model based on the reaction kinetics for hydrogen production from waste PE via steam gasification integrated with CO_2 capture has been presented. Temperature and steam/PE ratio has shown influence to the hydrogen purity and hydrogen yield. In a nutshell, this work has provided meaningful resources that can be used as a basis for more detail work for gasification of waste PE. It is also recommended that more study on gasification of waste PE need to be done with integration of in-situ CO_2 capture since there are strong potential of hydrogen production.

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